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Studies in the Development of North Dakota Lignite

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STUDIES IN THE DEVELOPMENT OF NORTH DAKOTA LIGNITE.

I. Further Studies on the Effect of Certain Inorganic Materials on the Low Temperature Carbonization of North Dakota Lignite.

II. The Effect of Certain Inorganic Materials on the Reactivity of the Char from North Dakota Lignite.

-by-

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This Thesis, presented by Arthur William Koth as a partial fulfillment of the requirements for the degree of Master of Science in the University of North Dakota, is hereby approved by the Committee in charge of his work.

Irvin Lavine

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INTRODUCTION.

There is a large area in the western part of the state which is underlain with lignite coal. The estimated (1) reserve of lignite in the United States is nine hundred sixty five billion tons. North Dakota alone has an estimated tonnage of over six hundred thirty three billion tons included in an area of twenty eight thousand square miles. This abundant supply, if properly developed and used, would supply North Dakota and its neighboring states for many generations.

Lignite is characterized by its high moisture content and high oxygen content in proportion to carbon. As mined it contains from 30 to 40 per cent moisture, when exposed to the atmosphere it loses about 50 per cent of its moisture. This loss is accompanied by slacking which limits the shipping radius and storing qualities.

Carbonization offers itself as a solution. Babcock and Odell (2) demonstrated that a good domestic fuel can be made from lignite by carbonization and subsequent briquetting with the addition of a foreign binder.

Gauger and Salley (3) studied the effect of various inorganic materials on the coking properties of North Dakota lignite. They found that "hydrates of aluminum chloride, sulfate and nitrate, magnesium sulfate and chloride and strontium chloride alter the structure of the char produced yielding a hard pseudo-coke differing materially from the soft powdered char of the untreated coal, whereas the anhydrous salts produce soft fine chars."

Gauger, Taylor, and Ulmen (4) studied the effects of blending and mechanical pressure on the coking of lignite.

A summary of their work,

1. Precarbonization of Dakota lignite at 450° C. eliminates most of the carbon dioxide.
2. Carbonization of the char from precarbonization of lignite mixed with Skelly pitch and certain bituminous coals yields a firm coke.
3. Mechanical pressure during carbonization has a marked effect on the structure of the solid residue.
4. Addition of aluminum chloride greatly aids the formation of coke residue.

Adams (5) studied the effect of drying on the products of low temperature carbonization of North Dakota lignite.

The present investigation is concerned with further study of inorganic materials influence on low temperature carbonization of Dakota lignite to extend the study to coals dried by the Fleissner method and determine the reactivity of the chars to oxygen.

Apparatus.

The set-up used in this investigation is similar to that used by Gauger and Salley (3) and is shown in Figures 1 and 2. The aluminum retort (J) is of the same type as used by Fischer (7) in his researches on the German coals. The retort was placed in the holder (B) which served as an insulator. A short water condenser (C) prevented the softening of the rubber connection to the off-take pipe of the retort. A 500 cc. round bottom flask (D) was used as a

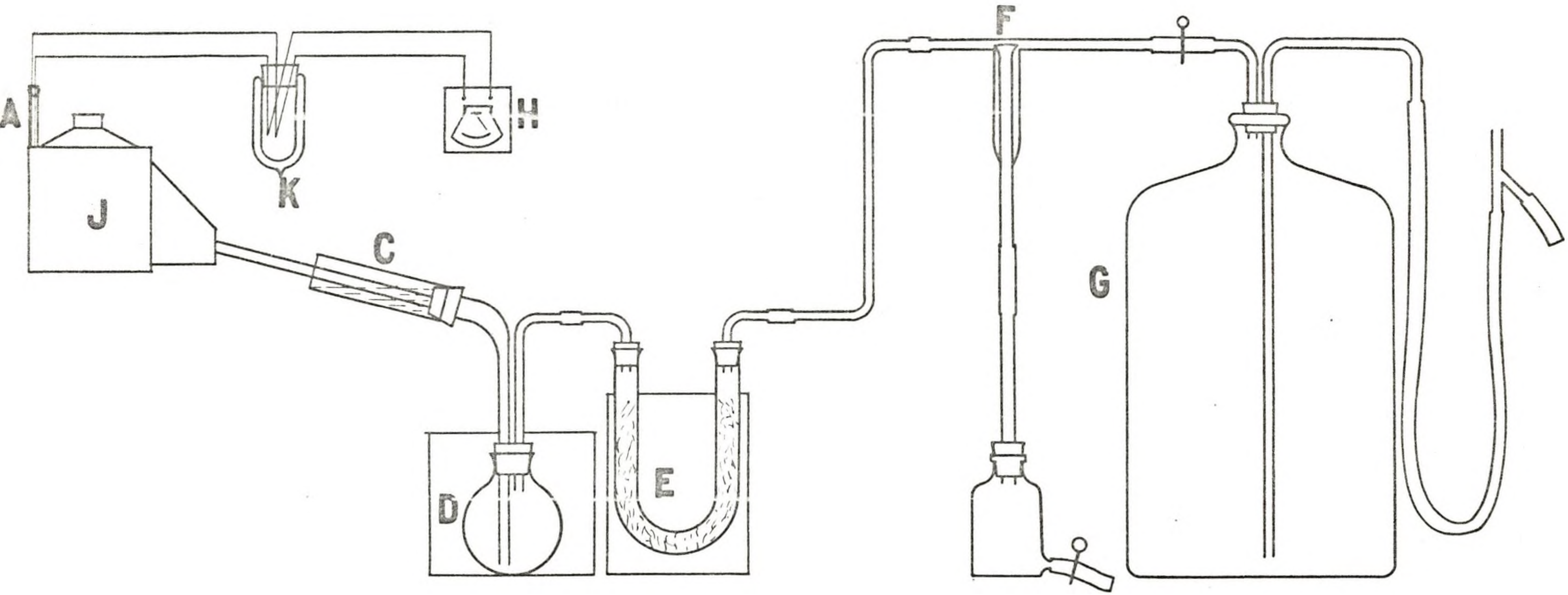

Fig. 1

Carbonization Apparatus

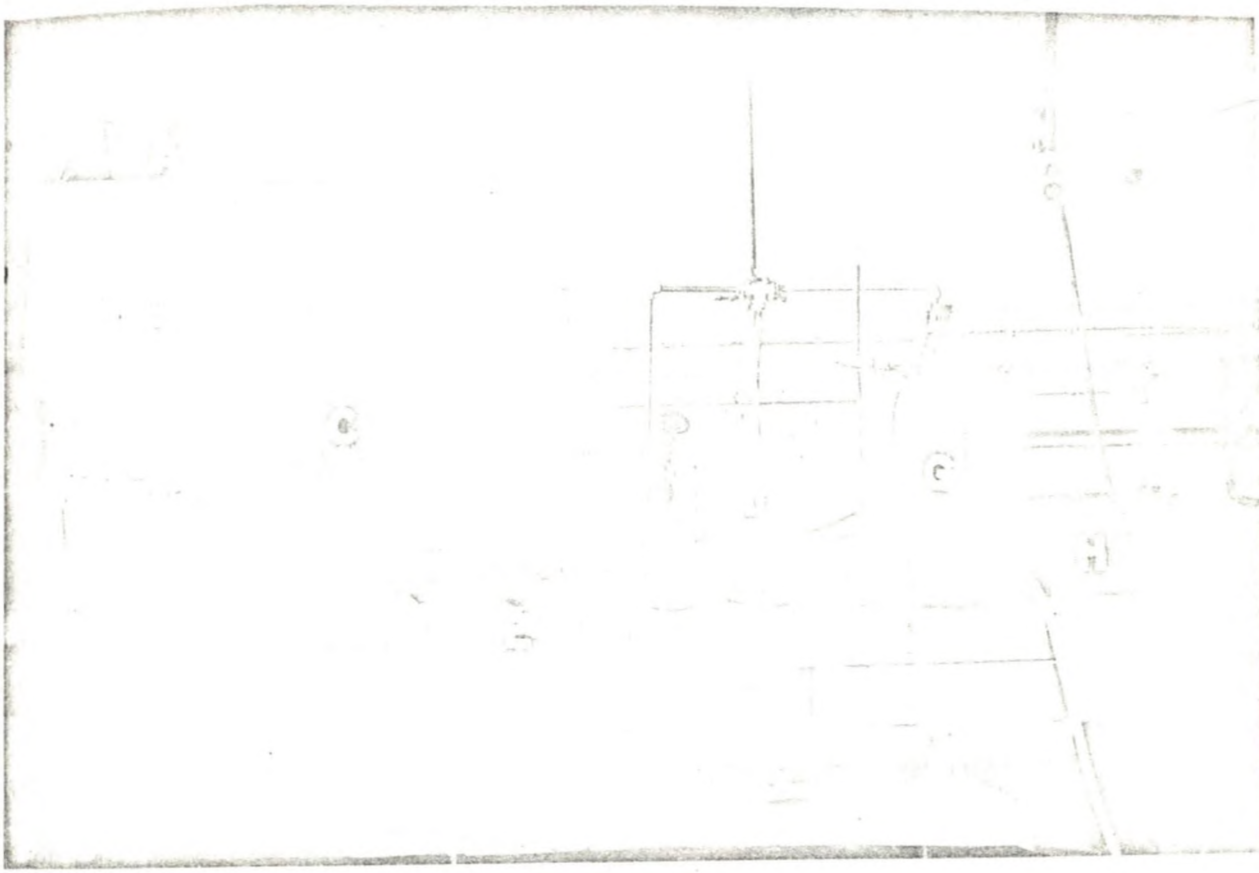

Fig. 2

Photograph of Carbonization Apparatus

condensing receiver, and was surrounded by an ice bath. The outlet tube from the condensing flask lead into the U tube (E) packed with glass wool and surrounded by an ice bath. From the filter the gas was lead through the sampling device (F) and to the calibrated aspirator bottle (G) filled with gas saturated water. The "Y" furnishes a means for keeping the pressure inside the bottle equal to atmospheric pressure.

A chromel-alumel thermocouple (A) and Leeds and Northrup potentiometer (H) were used to record the temperature. The thermocouple was calibrated against the freezing points of lead (327° C.), zinc (419° C.), and aluminum (659° C.). The cold junction (K) was kept at zero by an ice water mixture in a Dewar flask.

Procedure.

The iron chloride hydrate and magnesium chloride hydrate were dissolved in the proper amount of water and the solution added to the lignite. This mixture was ground up very intimately in a mortar. The more insoluable materials were added dry in the powdered form (through 150 mesh) and then mixed intimately with the lignite before the proper amount of water was added. In the work by Gauger and Salley (8) the reagents were all dissolved in water and the solution added to the lignite. They used a small foot-operated cypel machine in making the briquets. Since it is practically impossible to make the briquets under identical conditions their procedure was abandoned. In order that the results might be comparable the briquets, 1-11/16 inches in diameter and 1-1/4 inches in height, were made in a Riehle compression machine at a definite pressure. 4000 pounds were applied, which is equivalent to 1800 pounds per square inch. The purpose of making briquets was to prevent as much as possible the carrying over of find coal with the gas stream and to obtain a more intimate packing of the lignite particles and the added reagent. The briquets were placed in an aluminum basket and weighed and placed in the retort. The rest of the train was connected, after having obtained the weights of the flask and filter.

The retort was heated to 500° C. in fifteen minutes at as uniform a rate as possible. The temperature was then held at 500°-510° C. for one and one half hours. Upon completion of the heating the final volume of gas was recorded together with its temperature and the barometric pressure. A screw clamp was placed between the U tube and aspirator bottle. The flask and U tube were disconnected and weighed. The U tube was dried for one hour at 105° C. with a small steady current of air flowing through it. The weight after drying above the weight before the run was called tar.

The separation of the tar from the rest of the distillate is rather difficult because of the low yields in tar. The zylene distillation method employed by Gauger and Salley (3) proved unsatisfactory, because some fine coal dust is always carried over with the gas stream and in some cases considerable inorganic material distills with tar and water. The following method was finally adopted. The flask contents was poured into a 400 cc. beaker washing the flask well with zylene and evaporating to dryness. This residue was then extracted several times with zylene to dissolve the tar and filtered into a weighed beaker. The tar xylene solution was evaporated to dryness on steam bath and weighed. This weight of tar was added to the tar from the U tube and represents total tar.

The bottle receiving the solution from the aspirator was raised, a siphon started which forced the gas back through the sampling device. A 300 cc. sample was drawn into the mercury aspirator bottle during the time that about five liters of gas were expelled. This sample was analyzed in a United States Steel Corporation Modified Orsat apparatus as described in "Methods of the Chemists of the United States Steel Corporation for the Sampling and Analyses of Gases" (8).

After the retort had cooled the char was removed, weighed, and bottled. Proximate analyses were made on all chars.

Materials.

The lignite used in series A, mixture numbers 1 - 7, tables 4 to 8, was taken from the Truax-Traer mine at Velva, North Dakota. A large sample was allowed to air dry and then crushed to pass through a 20 mesh sieve and bottled in Mason jars.

For series B, two portions of Velva lignite were taken. After crushing through a 20 mesh sieve one sample was treated with hydrochloric acid, to remove the greater part of the ash, was washed free of soluble salts, air dried and bottled. This lignite was used in mixtures 8 - 9, tables 9 - 13. A second portion was treated twice with a 10 per cent solution of sodium hydroxide by placing on the steam bath for several days. The humates were filtered from the residue and precipitated with hydrochloric acid washed free of oluble salts, dried and bottled. The residue from the sodium ydroxide extract was washed free of soluble salts, dried, and ottled. The residue from this extraction was used mixture numbers 0 - 11, tables 9 - 13. The humic acid was used in mixture umber 12, tables 9 - 13.

In series C, Wilton lignite taken f rom the Truax-Traer mine t Wilton, North Dakota which had been previously dried by the 'leissner method (6). This lignite was used in mixture numbers 3 - 19, tables 14 - 18.

In series D, Velva lignite processed by the same method was ised in mixturesnumbers 20 - 26, tables 19 - 23.

TABLE 1.

Proximate analyses of the lignites used.

	H_2O	V.M.	F.C.	Ash
Velva lignite, series A	12.7	38.6	39.5	9.2
" " " B (acid washed)	7.9	44.7	45.7	1.7
" " " B (NaOH washed)	11.2	38.6	40.7	9.5
Wilton steam dried lignite, series C	10.5	44.5	41.5	3.5
Velva steam dried lignite, series D	13.3	39.6	39.8	7.3
Humic acid	2.3	44.5	53.9	2.3

The reagents whose effect was studied were sodium carbonate, aluminum sulfate hydrate, aluminum chloride hydrete, calcium carbonate, ferric chloride hydrate, and magnesium chloride hydrate.

For purposes of calculations the assumption made by Gauger and Salley (3) as to the compounds formed during carbonization from aluminum chloride and sulfate hydrate were used in the present

TABLE 2.

Composition of mixtures.

1. 142.5 g. Velva lignite, 30 g. H_2O
2. 142.5 g. " " , 7.5 g. Na_2CO_3, 28 g. H_2O
3. 142.5 g. " " , 54.3 g. $Al_2(SO_4)_3$ $18H_2O$, 28 g. H_2O
4. 142.5 g. " " , 15.97 g. MgCl $6H_2O$, 28 g. H_2O
5. 142.5 g. " " , 7.5 g. $CaCO_3$, 33 g. H_2O
6. 142.5 g. " " , 35.52 g. $AlCl_3 6H_2O$, 28 g. H_2O
7. 142.5 g. " " , 25.28 g. $FeCl_3 6H_2O$, 28 g. H_2O
8. 142.5 g. " " (acid washed), 30 g. H_2O
9. 142.5 g. " " (" "), 54.3 g. $Al_2(SO_4)_3 18\ H_2O$, 20 g. H_2O
10. 142.5 g. " " (NaOH washed), 30 g. H_2O
11. 142.5 g. " " (" "), 54.3 g. Al_2SO_4 18 H_2O, 20 g. H_2O
12. 142.5 g. " " , 14.25 g. humic acid, 30 g. H_2O
13. 142.5 g. Wilton steam dried lignite, 30 g. H_2O
14. 142.5 g. " " " " , 54.3 g. $Al_2(SO_4)_3$ 18 H_2O, 20 g. H_2O
15. 142.5 g. " " dried lignite, 7.5 g. Na_2CO_3, 28 g. H_2O
16. 142.5 g. " " " " , 25.28 g. $FeCl_3$ 6 H_2O, 28 g. H_2O
17. 142.5 g. " " " " , 7.5 g. $CaCO_3$, 33 g. H_2O
18. 142.5 g. " " " " , 15.97 g. $MgCl_2$ 6 H_2O, 28 g. H_2O
19. 142.5 g. " " " " , 35.52 g. $AlCl_3$ $6H_2O$, 25 g. H_2O
20. 142.5 g. Velva steam dried lignite, 30 g. H_2O
21. 142.5 g. " " " " , 7.5 g. $CaCO_3$, 33 g. H_2O
22. 142.5 g. " " " " , 25.28 g. $FeCl_3$ 6 H_2O, 28 g. H_2O
23. 142.5 g. " " " " , 15.97 g. $MgCl_2$ 6 H_2O, 28 g. H_2O
24. 142.5 g. " " " " , 7.5 g. Na_2CO_3, 28 g. H_2O
25. 142.5 g. " " " " , 35.52 g. $AlCl_3$ 6 H_2O, 20 g. H_2O
26. 142.5 g. " " " " , 54.5 g. $(Al_2SO_4)_3$ 18 H_2O, 20 g. H_2O

work. They assumed that these compounds form the oxide. During the progress of this work it was discovered that this is not the case for the aluminum sulfate hydrate. A fuller discussion is given later.

The ferric chloride hydrate was added as ferric oxide. Magnesium chloride hydrate was assumed to remain as the anhydrous salt. Calcium carbonate and sodium carbonate were assumed to remain unchanged.

Five per cent additions (based on compound formed) were made to the coal.

Table 2 gives the composition of mixtures used.

The lignite for all of the mixtures had the particle size given by mixture (1), Table 3, which was determined by experiment.

The effect of particle size on the appearance of the char.

The catalytic coking of lignite being merely a cementing of the carbonized particles it was thought that particle size might exert a definite influence upon the pseudo-coke produced. A series of runs were made using mixture 6, Table 2. Table 3 gives the mixtures of particle size employed and a brief description of the cokes obtained. The carbonization of any of the individual sizes did not produce a good coherent coke also, if particles larger than 20 mesh were used the product was inferior and unsatisfactory. Mixture (1) gave the best results. Its hardness and good cementing as viewed under the microscope sets it aside from the rest. This blend was used throughout this work.

TABLE 3.

Mixture	-20+40	-40+60	-60+80	-80+100	-100+150	-150+200	-200
(a)	50%	15%	10%	---	---	---	25%
	Poor coke, cracked badly and soft.						
(b)	50%	15%	---	---	---	---	35%
	Very soft.						
(c)	30%	30%	10%	---	10%	---	30%
	Fair appearance but easily rubbed down in interior.						
(d)	30%	30%	10%	---	---	---	30%
	Badly cracked and very crumbly.						
(e)	40%	15%	5%	5%	5%	5%	25%
	Few cracks, otherwise good appearance, crumbly center.						
(f)	50%	---	5%	5%	5%	5%	30%
	Badly cracked and interior uncemented and soft.						
(g)	10%	30%	5%	5%	5%	5%	40%
	Hard but very badly cracked.						
(h)	5%	35%	10%	10%	10%	10%	20%
	Badly cracked and quite soft.						
(i)	40%	16%	6%	5%	5%	5%	23%
	Single horizontal crack. Very hard, gray metallic luster and appeared well cemented under microscope.						

Series A.

TABLE 4.

Proximate analyses of chars.

Mixture No.	Dry basis. V.M.	F.C.	Ash	Dry and ash free basis V.M.	F.C.
1	17.90	67.43	14.67	20.93	79.07
1	17.70	67.57	14.73	20.77	79.23
2	17.79	63.04	19.17	22.15	77.85
2	19.05	61.68	19.27	23.60	76.40
3	23.40	53.45	23.15	30.50	69.50
3	22.50	54.00	23.50	29.40	70.60
4	13.55	70.08	16.37	16.21	83.79
4	13.80	69.57	16.85	16.60	83.40
5	20.50	60.90	18.60	25.18	74.82
5	21.21	60.63	18.16	25.92	74.08
6	13.93	65.00	21.07	17.66	85.34
6	13.69	67.59	19.72	16.84	83.16
7	13.67	64.95	21.38	17.38	82.62
7	13.65	67.65	18.70	16.79	83.21

TABLE 5.

Yield of char, tar, and gas per 100 grams of moisture and ash free lignite taken.

Mixture No.	Grams of char dry and ash free	Grams of tar	Liters of gas N.T.P.
1	64.8	3.25	12.4
1	65.4	3.72	12.3
2	55.4	3.71	15.3
2	56.2	3.27	14.9
3	73.0	3.28	14.8
3	72.6	3.55	14.0
4	68.3	3.01	13.4
4	68.4	3.47	14.6
5	67.0	3.20	14.6
5	61.2	3.54	14.2
6	69.2	3.47	14.9
6	70.1	2.77	14.5
7	67.9	2.20	15.3
7	64.4	2.27	13.6

Table 6

Percentage Deviation from blank for the reagent

Mixture No.	Char	Tar	Gas
1	0.0	0.0	0.0
2	+ 0.8	+ 0.3	+ 22.7
3	+ 12.1	- 2.0	+ 17.9
4	+ 4.5	- 6.9	+ 13.8
5	+ 5.0	- 2.6	+ 17.9
6	+ 7.3	-10.3	+ 18.7
7	+ 8.4	-38.5	+ 14.6

TABLE 6.

Percentage deviation from blank for the reagent.

Mixture number	Char	Tar	Gas
2	- 14.3	0.3	20.7
3	11.8	- 0.6	12.9
4	5.0	- 6.9	13.4
5	- 1.4	- 3.1	16.7
6	7.1	-10.3	19.0
7	6.1	-35.3	17.0

TABLE 7.

Gas analyses and heating value.

Mixture number	CO_2	Ill	O_2	H_2	CO	C_2H_6	CH_4	B.t.u. per cu. ft. calculated.
1	53.1	3.6	1.2	7.0	3.1	3.6	24.6	357
1	55.2	3.3	1.1	7.3	3.4	4.75	25.1	375
2	49.7	3.1	2.2	9.3	1.4	2.0	23.8	319
2	54.0	2.6	1.1	6.8	1.7	1.6	25.7	315
3	64.8	2.7	2.6	2.7	2.7	6.7	20.9	348
3	65.0	2.4	1.6	3.2	2.1	5.8	21.2	327
4	53.6	3.6	1.2	7.0	2.2	3.6	24.6	352
4	51.7	2.7	1.5	7.3	2.0	2.1	25.7	324
5	50.1	4.0	2.1	5.4	1.6	6.2	27.0	414
5	52.7	3.1	1.8	5.0	2.4	4.8	26.1	372
6	45.7	4.8	6.4	5.1	2.8	5.8	26.6	418
6	47.3	3.2	1.9	7.2	3.2	5.1	21.1	342
7	53.4	3.4	1.9	8.7	1.4	1.0	25.4	318
7	51.2	2.5	1.5	9.8	1.6	0.6	24.3	291

TABLE 8.

Screen analyses of chars.

Mixture number	-20 +40 %	-40 +60 %	-60 +80 %	-80 +100 %	-100 +150 %	-150 +200 %	-200 %
1	31.8	20.6	10.0	8.8	6.8	1.8	20.7
1	29.4	25.5	9.4	8.5	6.9	0.5	21.5
2	44.8	21.8	7.4	5.8	4.6	1.3	14.0
2	45.6	22.5	7.2	5.8	4.5	0.4	13.7
3	49.0	20.2	7.2	5.5	4.5	0.5	13.0
3	47.2	20.8	7.4	5.8	4.7	0.4	13.8
4	29.8	22.9	10.2	8.2	6.4	1.5	20.2
4	29.1	19.2	8.7	7.9	6.8	0.4	27.6
5	31.6	19.7	8.2	7.6	6.5	1.7	24.6
5	33.3	18.7	8.5	7.8	6.4	1.7	23.4
6	40.1	19.5	7.5	6.4	5.8	0.45	20.4
6	45.7	20.7	7.0	5.5	4.6	1.0	15.2
7	46.5	22.6	7.54	5.4	4.2	0.3	13.7
7	[illegible]	21.6	7.20	5.6	4.0	0.2	11.2

Series B.

TABLE 9.

Proximate analyses of chars from washed coals.

Mixture number	V.M.	F.C.	Ash	V.M.	F.C.
8	17.4	79.4	3.2	18.3	81.7
9	22.4	64.2	13.4	25.9	74.1
10	17.2	67.7	15.0	20.2	79.8
11	20.1	54.9	25.0	26.8	73.2
12	16.6	68.3	15.1	21.4	78.6

TABLE 10.

Yield of char, tar, and gas per 100 grams of dry and ash free lignite taken.

Mixture number	Grams of char dry and ash free	Grams of tar	Liters of gas N.T.P.
8	55.4 62.5	3.35 3.65	10.6 11.6
9	66.5 74.6	3.01 3.45	11.2 12.7
10	55.7 62.7	2.87 3.24	12.2 13.8
11	60.7 68.4	1.90 2.15	11.1 12.3
12	~~65.9~~ 73.1	~~3.11~~ 3.57	~~10.6~~ 12.1

TABLE 11.

Percentage deviation from blank

Mixture number	Char	Tar	Gas
9	19.6 +19.4	~~-10.3~~ -5.5	5.5 +8.7
11	9.0 + 9.1	~~-23.8~~ -33.6	~~-9.2~~ -10.9
12	~~-1.8~~ +13.1	~~-10.6~~ +2.6	~~-14.5~~ -1.6

Table 12.

Gas analyses and heating value.

Mixture number	CO_2	Ill	O_2	H_2	CO	C_2H_6	CH_4	B.T.U. per cu. ft. calc.
8	46.8	3.5	1.8	5.2	5.2	10.9	26.3	484
9	59.1	3.0	1.4	3.6	2.0	6.2	18.9	323
10	51.6	2.7	1.9	7.3	1.5	4.6	23.4	340
11	69.4	3.8	0.6	5.4	1.1	3.3	17.0	274
12	45.7	3.1	1.3	8.1	7.6	5.7	24.7	397

68.8

Table 13.

Screen analyses of chars from washed coals.

Mixture number	-20 40 %	-40 60 %	-60 80 %	-80 100 %	-100 150 %	-150 200 %	-200 %
8	33.6	23.6	11.0	8.8	6.5	1.1	15.2
9	65.8	20.0	7.5	6.7	5.6	0.6	13.8
10	34.2	25.6	9.1	8.4	6.8	0.7	17.2
11	40.8	25.5	7.9	6.8	5.7	0.9	14.2
12	55.5	25.3	8.7	7.6	5.4	1.2	15.9

35.5 6

Series C.

TABLE 14.

Proximate analyses of Wilton steam dried chars.

Mixture bumber	Dry V.M.	Dry F.C.	Dry Ash	Dry and ash free V.M.	Dry and ash free F.C.
13	16.6	77.9	5.5	17.6	82.4
14	21.8	~~65.6~~ 63.2	~~12.6~~ 15.0	24.9	75.1
15	17.7	~~67.3~~ 69.7	~~15.0~~ 12.6	20.9	79.1
16	13.2	74.1	12.7	15.1	84.9
17	20.2	70.1	~~9.7~~ 9.7	22.4	77.6
18	14.2	76.8	9.0	15.6	84.4
19	13.8	73.4	12.8	15.9	84.1

TABLE 15.

Yield of char, tar, and gas per 100 grams of dry and ash free lignite taken.

Mixture number	Grams of char dry and ash free	Grams of tar	Liters of gas N.T.P.
13	~~61.7~~ 63.7	~~1.45~~ 1.49	~~11.5~~ 11.8
14	~~72.2~~ 74.4	~~1.50~~ 1.55	~~11.8~~ 12.1
15	~~61.2~~ 64.7	~~1.25~~ 1.29	~~12.5~~ 12.9
16	~~67.0~~ 69.1	~~0.76~~ 0.79	~~11.1~~ 11.5
17	~~64.3~~ 67.1	~~2.59~~ 2.67	~~11.0~~ 11.3
18	~~64.2~~ 66.2	~~2.18~~ 2.25	~~11.0~~ 11.3
19	~~64.7~~ 66.6	~~1.33~~ 1.37	~~12.2~~ 12.6

TABLE 16.

Percentage diviation from blank.

Mixture Number	Char	Tar	Gas
14	~~17.0~~ +16.8	~~5.4~~ + 4.0	~~2.6~~ +2.6
15	~~- 0.8~~ + 1.6	~~- 13.8~~ -13.4	~~8.7~~ +9.3
16	~~8.6~~ + 8.5	~~- 47.6~~ -47.0	~~- 3.5~~ - 2.5
17	~~- 4.4~~ + 5.3	~~64.8~~ +79.2	~~- 4.5~~ -4.3
18	~~- 4.5~~ + 3.9	~~50.4~~ +51.0	~~- 4.3~~ -4.3
19	~~- 4.9~~ + 4.6	~~- 8.3~~ - 8.1	~~6.1~~ + 6.8

TABLE 17.

Gas analyses and heating value.

Mixture number	CO_2	Ill	O_2	H_2	CO	C_2H_6	CH_4	B.t.u. per cu. ft. calc.
13	33.7	3.0	1.6	14.0	13.9	2.1	26.6	392
14	53.1	1.9	1.7	8.7	8.6	2.0	25.3	331
15	46.6	2.0	0.9	16.4	7.1	1.3	25.4	338
16	32.0	3.1	1.5	19.4	10.5	3.7	32.1	470
17	38.9	2.4	0.9	7.8	7.4	9.7	23.0	432
18	34.8	3.8	1.4	11.7	15.2	5.2	24.7	431
19	22.0	3.9	3.0	18.2	11.9	2.5	22.8	391

TABLE 18.

Screen analyses of Wilton steam dried chars.

Mixture number	-20 40 %	-40 60 %	-60 80 %	-80 100 %	-100 150 %	-150 200 %	-200 %
13	34.8	20.5	8.7	8.7	7.7	1.4	18.3
14	52.8	18.5	6.4	5.6	4.5	1.2	11.0
15	35.4	25.2	11.2	7.7	6.0	1.8	12.4
16	32.3	19.8	9.4	7.9	6.8	1.4	22.4
17	44.8	24.6	9.7	9.8	9.0	1.7	40.7
18	41.3	20.1	7.8	6.7	5.2	4.9	14.0
19	36.4	16.8	9.5	8.8	8.4	8.0	12.1

Series D.

TABLE 19.

Proximate analyses of Velva steam dried.chars.

Mixture number	Dry basis V.M.	F.C.	Ash	Dry and ash free V.M.	F.C.
20	18.2	69.8	12.0	20.7	79.3
21	20.1	64.9	15.0	23.6	76.4
22	13.6	68.4	18.0	16.5	83.5
23	13.5	71.7	14.8	15.9	84.1
24	18.6	64.3	17.1	22.4	77.6
25	14.1	67.7	18.2	17.3	82.7
26	21.8	54.7	23.4	28.4	71.6

TABLE 20.

Yield of char, tar, and gas per 100 grams of dry and ash free lignite.

Mixture number	Grams of char dry and ash free	Grams of tar	Liters of gas N.T.P.
20	65.5	1.84	12.6
21	67.2	1.89	~~12.0~~ 11.8
22	68.9	1.25	12.7
23	70.9	1.52	12.4
24	~~64.9~~ 65.0	1.23	13.6
25	~~68.8~~ 68.5	1.68	10.5
26	~~70.0~~ 69.8	1.19	10.2

TABLE 21.

Percentage deviation from blank.

Mixture number	Char	Tar	Gas
21	~~2.9~~ +2.6	~~3.2~~ +2.7	~~-4.7~~ -6.3
22	~~5.1~~ +5.2	~~-31.6~~ -32.1	0.6 + 0.8
23	~~8.4~~ +8.2	~~-17.5~~ -17.5	~~-1.6~~ -1.6
24	~~-0.6~~ -0.8	~~-33.3~~ -33.2	~~12.7~~ +7.9
25	~~5.4~~ +4.6	~~-8.2~~ -8.7	~~-16.7~~ -16.7
26	~~7.3~~ +6.6	~~-35.6~~ -35.5	~~-19.8~~ -19.1

TABLE 22.

Gas analyses and heating value.

Mixture number	CO_2	Ill.	O_2	H_2	CO	C_2H_6	CH_4	B.t.u. per cu. ft. calc.
20	48.8 ~~50.1~~	3.2	1.0	10.6	9.8	1.1	25.5	342
21	~~42.0~~ 52.9	2.3	0.9	14.0	7.0	0.7	19.8	278
22	51.2	1.8	1.1	16.6	8.4	2.3	15.4	289
23	53.0	3.5	1.0	9.8	9.7	4.6	16.7	306
24	56.0	2.9	0.7	12.9	5.1	3.0	18.2	300
25	42.3	3.3	1.2	9.5	10.2	6.1	19.7	373
26	~~66.9~~ 65.1	2.5	0.9	6.8	9.6	3.5	11.6	237

TABLE 23.

Screen analyses of Velva steam dried chars.

Mixture number	-20 40 %	-40 60 %	-60 80 %	-80 100 %	-100 150 %	-150 200 %	-200 %
20	34.6	22.1	8.9	8.4	7.0	1.7	17.3
21	30.2	14.9	7.6	7.3	7.3	7.5	25.3
22	37.8	18.4	8.2	6.4	5.6	5.6	18.0
23	36.2	17.8	8.2	7.1	6.5	6.2	18.0
24	49.5	26.3	7.1	5.0	3.8	3.1	5.2
25	61.1	23.6	8.2	6.6	5.1	5.0	13.8
26	56.3	17.0	6.0	4.9	4.4	2.7	7.6

Results:

The yields of char, tar, and gas are all reported as yields per 100 grams of dry and ash free char. Tables 3 - 23 give a complete summary of the results from all of the carbonization experiments.

The char were examined by

1. Appearance
2. Reactivity (Part 2)
3. Screen analysis.

Discussion: Raw coals chars.

The chars from sodium carbonate, calcium carbonate, and magnewium chloride hydrate did not show any evidence of coking. The briquets had retained their form when the retort was opened, but when tauched they crumbled into a mass with no noticeable difference from the blank runs. Calcium carbonate has the tendency to produce much fine material in the char as is indicated by Table 8 when compared with blank runs. Gauger and Salley (3) found that magnesium chloride hydrate alters the structure, but they added the salt on the oxide basis and hence used a much larger weight proportion of the salts.

The addition of ferric chloride hydrate causes no apparent evidence of coking other than the production of a much smaller amount of fines when compared with the blank run. Sutcliffe and Cobb (10) find that the addition of 1 and 3 per cent of ferric oxide to a coking coal causes the coke to be very soft and friable.

Aluminum chloride hydrate and aluminum sulfate hydrate produced a very hard residue which was named pseudo coke by Guager and Salley (3). The core of the char briquets was somewhat softer than the outside and did not have the gray metallic luster exhibited further toward the surface, yet under the mixroscope the coked lignite particles appeared well cemented through the entire briquet. The pseudo coke obtained from mixture (9) exhibited the greatest hardness and finest structure.

Tables 9 - 13 mixtures 8 - 9 sum up the results obtained when the coal was washed with hydrochloric acid. Evidently the washing with hydrochloric acid removed some of the inorganic materials which retard the action of the catalyst.

Tables 9 - 13 show the results obtained with alkali extracted coal and the addition of humic acid. Lignite extracted with a 10 per cent sodium hydroxide solution and carbonized with out addition of inorganic salts yields a char that does not differ from that obtained from blank run with freshly mined coal. When this lignite is carbonized with the aluminum sulfate mixture (11) the usual effect of this salt is practically destroyed, for there is but slight evidence of any coking. Evidently the greater part of the organic material upon which this salt acts has been removed or probably hydrolized.

Steam dried chars.

Tables 14 - 23 give the results for the carbonization of steam dried lignite in the presence of the various salts previously utilized.

The Velva steam dried chars for each salt added had the same physical appearance as was evidenced when similar experiments were performed with freshly mined coal with the single exception of the salt aluminum chloride hydrate. This salt did not produce the marked effect it produced with the freshly mined coal in that the briquets were badly cracked, considerable softer, and did not exhibit a gray metallic luster.

In the case of the Wilton steam dried lignite tables 14 - 18 the addition of sodium carbonate, calcium carbonate, and magnesium chloride hydrate produced chars that in physical appearance were similar to the chars obtained with Velva freshly mined coal. However, ferric chloride hydrate showed a decided effect toward coking. This salt produced a char which was considerably better than the one produced by the addition of aluminum chloride hydrate, a phenomenon just opposite to that obtained with the freshly mined coal. Aluminum sulfate, although it produced a firm briquet, did not have the hardness or the well cemented appearance under the microscope that the similar briquet from Velva lignites exhibited.

Gas and Tar yields:

In Tables 5, 6, 10, 11, 15, 16, 20 and 21 there are listed the yields of tar and gas for various experiments as well as the percentage deviation from the blank for experiments in each series.

An inspection of these tables shows that sodium carbonate cause a decrease in char and tar yields and increases the gas yield in all of the coals investigated except in the case of the raw coal. In this case the tar yield shows a slight increase over that obtained with the blank run.

Ferric chloride hydrate causes an increase in char yield and a very decided decrease in tar yields.

In making a comparison of steam dried Velva lignite with freshly mined Velva lignite it is found from data given in Tables 5 and 20 that with the former there is a decrease in tar of about 50 per cent and the gas yield is decreased by more than 15 per cent for each of the salts investigated. The analyses of the gas (Table 7 and 22) show a higher percent of hydrogen and carbon monoxide with a smaller quantity of methane for the steam dried lignite for each of the salts investigated.

The carbon dioxide content with the steam dried coal is practically the same as obtained with the freshly mined coal for a given salt, but varies considerable with different salts. The most striking examples are shown in case of aluminum chloride and aluminum sulfate hydrate. The former gives a decrease of 15 per cent for Velva and 30 per cent for Wilton coal while the latter gives an increase of 20 per cent for Velva and 60 per cent for the

Wilton coal when compared with the blank for that series.

Proximate Analyses:

There seems to be very little variation in the proximate analyses between chars from freshly mined and steam dried lignite for any given salt added (Table 4 and 19).

The aluminum sulfate char which was found to give a much higher volatile matter and ash content was investigated further. Sulfur analyses on char, volatile matter residue, and ash residue for a blank (mixture 20) and the aluminum sulfate (mixture 26) gave the following results.

	Blank (mixture 20)	$Al_2(SO_4)_3 18H_2O$ (mixture 26)
Char	0.36%	9.2%
Volatile residue	0.32%	4.7%
Ash residue	0.33%	2.2%

This indicates that all of the sulfur added as $Al_2(SO_4)_3 18H_2O$ remained in the char, but does not indicate as to its form. Probably it is bound with some organic matter as a double salt.

Summary:

1. Inorganic salts exert a definite effect on the structure of the chars as well as yields of char, tar, and gas from the low temperature carbonization of lignite.

2. Hydrates of aluminum chloride and aluminum sulfate produce pseudo cokes.

3. Drying by the Fleissner method influences the yields of tar, char, and gas as well as the analyses of the gases.

PART 2.

The effect of certain inorganic materials on the reactivity of the chars from North Dakota lignite.

INTRODUCTION.

Various methods have been proposed for measuring the reactivity of coke. The term reactivity as applied to coke lacks a definite meaning. With one group of investigators it is measured by such chemical reactions as decomposition of steam or carbon dioxide at elevated temperatures, while another group will use the oxidation reaction with air or oxygen. The latter is the basis of the present investigation.

Carbon and oxygen begin to react at a definite temperature. When this temperature is attained the rate of reaction is accelerated and this phenomenon can be utilized in differentiation the reactivity of cokes or chars. In the study of coals Wheeler (12) designates this point as the "relative ignition temperature," Parr and Coons (13) term this the "critical oxidation temperature."

Bunte (14) defines the reactivity of a coke in terms of its ignition temperature determined in air under a set of fixed conditions.

Bähr (15) passed oxygen and air through a definite volume of granulated coke at 850° - 950° C. and analyzed the resulting gases. He found that the ratio of $CO:CO_2$ is increased by the presence of iron or iron oxide in the coke.

Fisher, Breuer, and Broche (16) passed carbon dioxide over the coke heated at a constant rate and termed the point at which carbon monoxide appeared the burning point.

Sherman and Kinney (17) streamed oxygen over a definite weight of coke at a definite temperature. The loss in weight after a given time was taken as a measure of reactivity. They found that the rate of combustion of coke in oxygen was not greatly influenced by coking time, porosity, volatile matter, specific gravity, or coking temperature. However, they add that particle size alone had a marked effect. These facts have been criticized by Korevaar (20).

Dent and Cobb (19) find that at 800° C. the pure coke and cokes prepared by addition of fine pepcent (calculated as oxide) of sodium carbonate, calcium carbonate, and ferric oxide show the rate of combustion when oxygen is passed over the coke surface.

Moore and Nevel (18) give information on the specific effects of the mineral constituents of coal and coke on the reactivity in oxygen nitrogen mixture and give quantitative data for certain fixed conditions.

Experimental.

Apparatus:

The apparatus used was essentially that used by Eaton, Brady, Gauger, Lavine, and Mann (9) and is shown in Figures 3 and 4. Oxygen from the tank (A) is passed successively through wash bottles (B) the first containing a 40 per cent solution of potassium, hydroxide, the second being empty to aid in flow, and the third containing concentrated sulfuric acid. The calcium chloride tower (C) is inserted to insure complete drying of the gas. A calibrated flow meter consisting of the capillary tube (E) and manometer (D) was employed to deliver oxygen at a constant rate. The gas then passed into the combustion tube (K) in furnace (F). The exit gases were cooled by flowing through a water cooled conden-

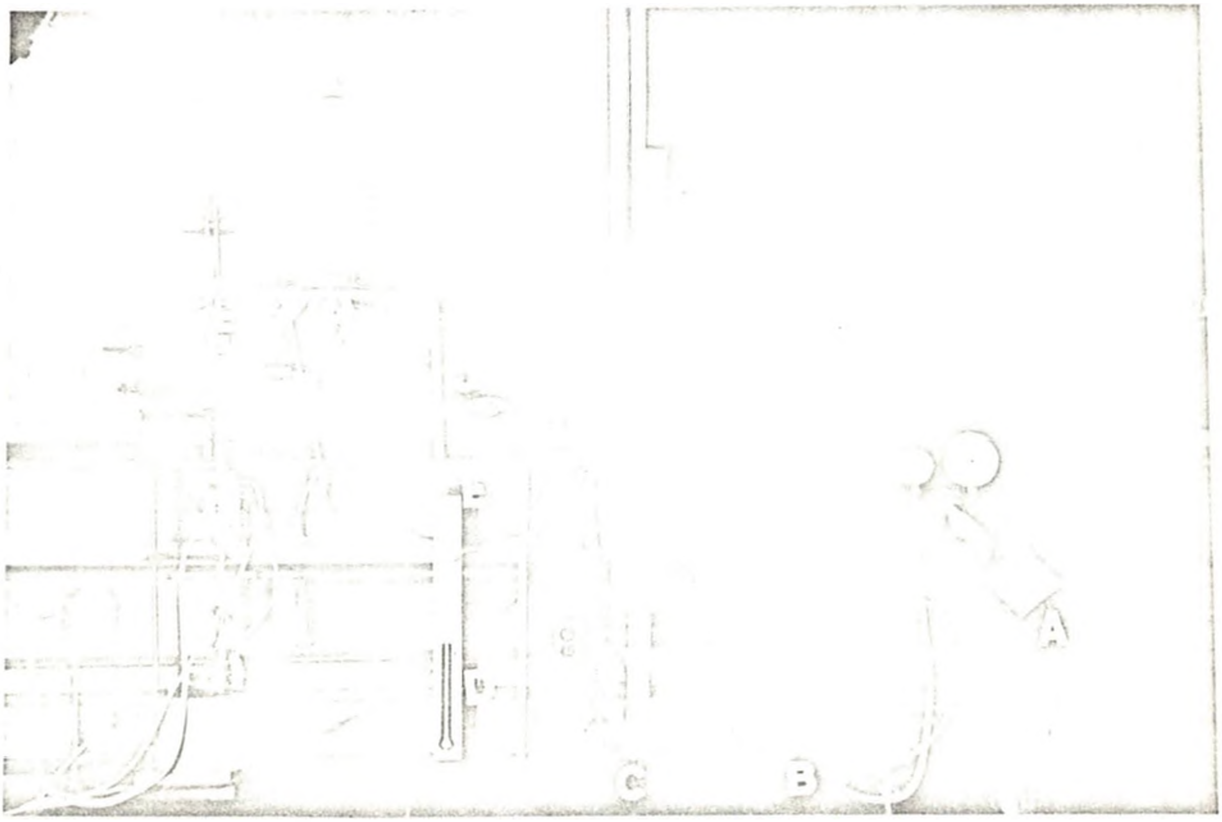

Fig. 4

Apparatus for Determing the Reactivity of Lignite Chars

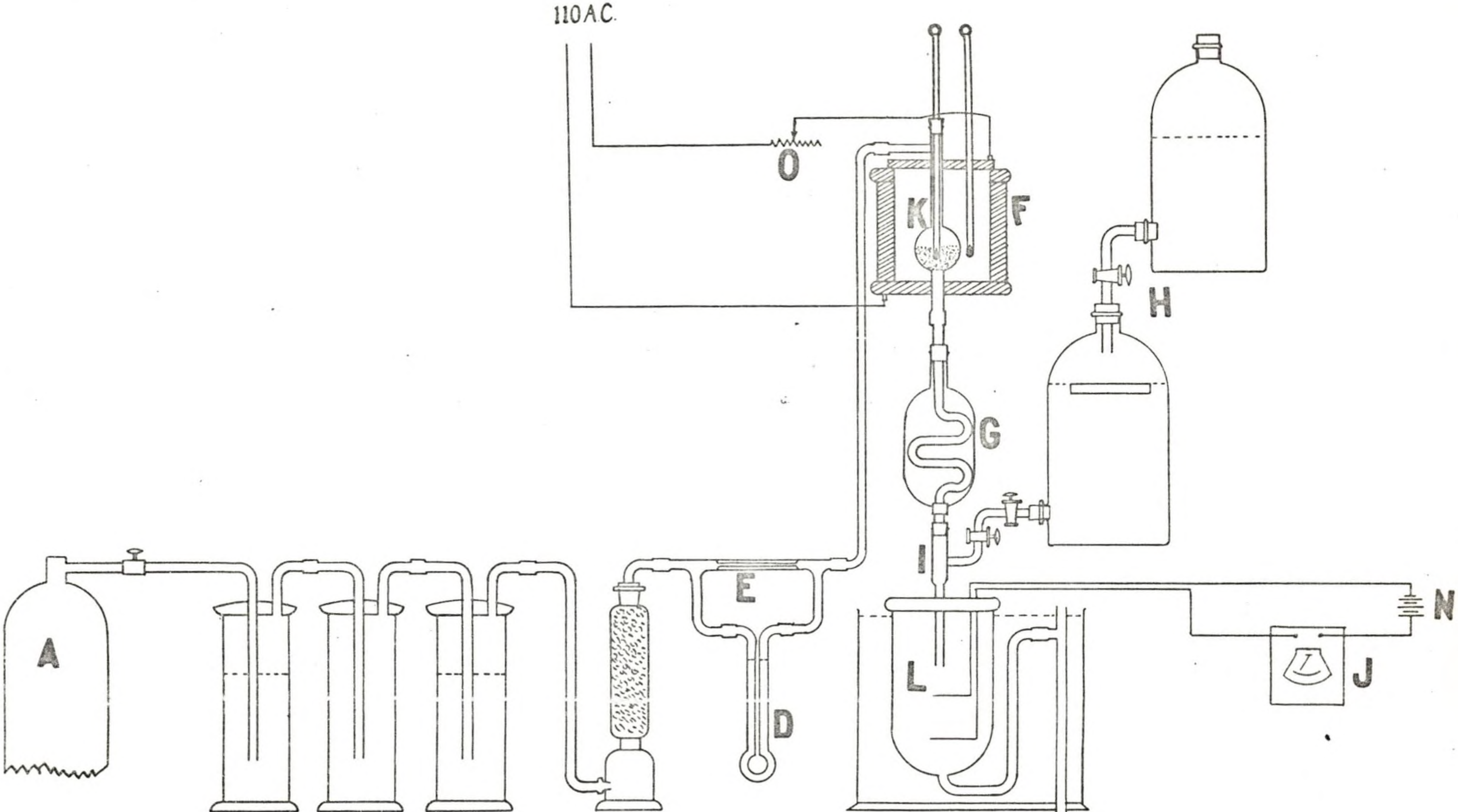

Fig 5
Reactivity Apparatus

ser (G) and into the mixing chamber (I) where they came ihto contact with the ammonium hydroxide solution. Conductivity cell (L) was made of 1½ inch glass tubing and fitted with gold platinized electrodes 1.5 cm. in diameter and 1.5 cm. apart. These electrodes were connected in series with two six volt storage batteries (N) and a miliammeter (J). The two bottles at (H) were used to deliver at a constant rate the ammonium hydroxide solution. The upper being merely a reservoir from which solution was drawn from time to time to keep the head constant in the lower bottle. The furnace (F) connected to 110 A.C. line is in series with a rheostat (O) used to control the temperature of the furnace.

Two 200° C. nitrogen filled thermometers were used to indicate the temperature of furnace and coal. The accuracy of both thermometers was checked against a Bureau of Standards calibrated thermometer.

Procedure.

The chars taken from the aluminum retort (Part 1) were crushed to pass thru a 20 mesh screen and immediately bottled to prevent oxidation in air as well as absorption of moisture. A portion was taken for screen analysis as a check on the particle size.

25 cc. of the char was placed in the combustion tube within the furnace, which was heated at the rate 2.5° C. per minute. Connection was then made to the oxygen supply coming from the tank through the wash bottles and metering device. Oxygen at the rate of 75 cc. per minute was passed through the coal. A 0.1 normal

solution of ammonium hydroxide was continually flowing into the mixing chamber at the rate of 20 cc. per minute. The mechanism of the carbon dioxide indicating system may be stated as follows: Pure oxygen has no effect on the conductivity of the ammonium hydroxide solution but any carbon dioxide present will be absorbed and the conductivity of the solution increases in direct proportion to the amount absorbed. With gas flowing at the rate of 75 cc. per minute it was calculated that there was about one minute interval from the time the gas left the combustion tube until it entered the cell. The carbon dioxide point on the time temperature curve is taken one minute back of the point at which it was first observed.

The coal temperature, furnace temperature, and milliamperes of current through the cell were recorded at two minute intervals.

Previous work with this apparatus (9) indicated that it was difficult to reproduce results obtained, which was probably due to high moisture in coal and shrinkage which accompanied the moisture loss. In the present investigation the check runs agree very closely, there being practically no moisture present and no noticeable shrinkage.

TABLE 24.

Crossing and CO_2 temperatures from raw Velva chars,

Series A.

ixture umber	Crossing temperature °C. Individual	Average	CO_2 temperature °C. Individual	Average
1	103		107	
	105		101	
	102		108	
	106	104	105	105
2	82			
	80		122	
	84		120	
	80	81.5	118	120
3	162		135	
	160		126	
	158	160	124	128
4	135		142	
	136		142	
	135		141	
	136	135.5	145	142.5
5	90		116	
	91		120	
	92		120	
	94	92	109	116
6	144		154	
	144		147	
	143		146	
	141	143	151	149.5
7	135		148	
	136		147	
	137		135	
	135	136	148	144.5

TABLE 25.

Crossing and CO_2 temperatures from washed Velva lignite chars, Series B.

Mixing number	Crossing temperature °C Individual	Average	CO_2 temperature °C. Individual	Average.
8	154		134	
	156	155	129	131.5
9	170		150	
	172	171	152	151
10	118		131	
	120	119	134	132.5
11	156		117	
	159	157.5	116	116.5
12	117		97	
	118	117.5	108	102.5

TABLE 26.

Crossing and CO_2 temperatures for the chars from Wilton Steam Dried lignite, Series C.

Mixture number	Crossing temperature °C. Individual	Average	CO_2 temperature °C. Individual	Average.
13	132		112	
	133	132.5	115	113.5
14	146		126	
	149	147.5	123	124.5
15	92		134	
	97	94.5	126	130.0
16	150		133	
	150	150.0	136	134.5
17	122		95	
	114	118.0	89	92.0
18	146		124	
	140	143.0	125	124.5
19	158		134	
	155	156.5	126	130.0

TABLE 27.

Crossing and CO_2 temperatures for the chars from Velva steam dried lignite, Series D.

Mixture number	Crossing temperature °C. Individual	Agerage	CO_2 temperature °C. Individual	Agerage
20	108		95	
	110	109.0	97	96.0
21	111		104	
	112	111.5	105	104.5
22	140		135	
	143	141.5	128	131.5
23	141		128	
	147	144.0	135	131.5
24	104		130	
	113	108.5	130	130 .0
25	161		144	
	160	160.5	141	142.5
26	163		98	
	160	161.5	102	105.0

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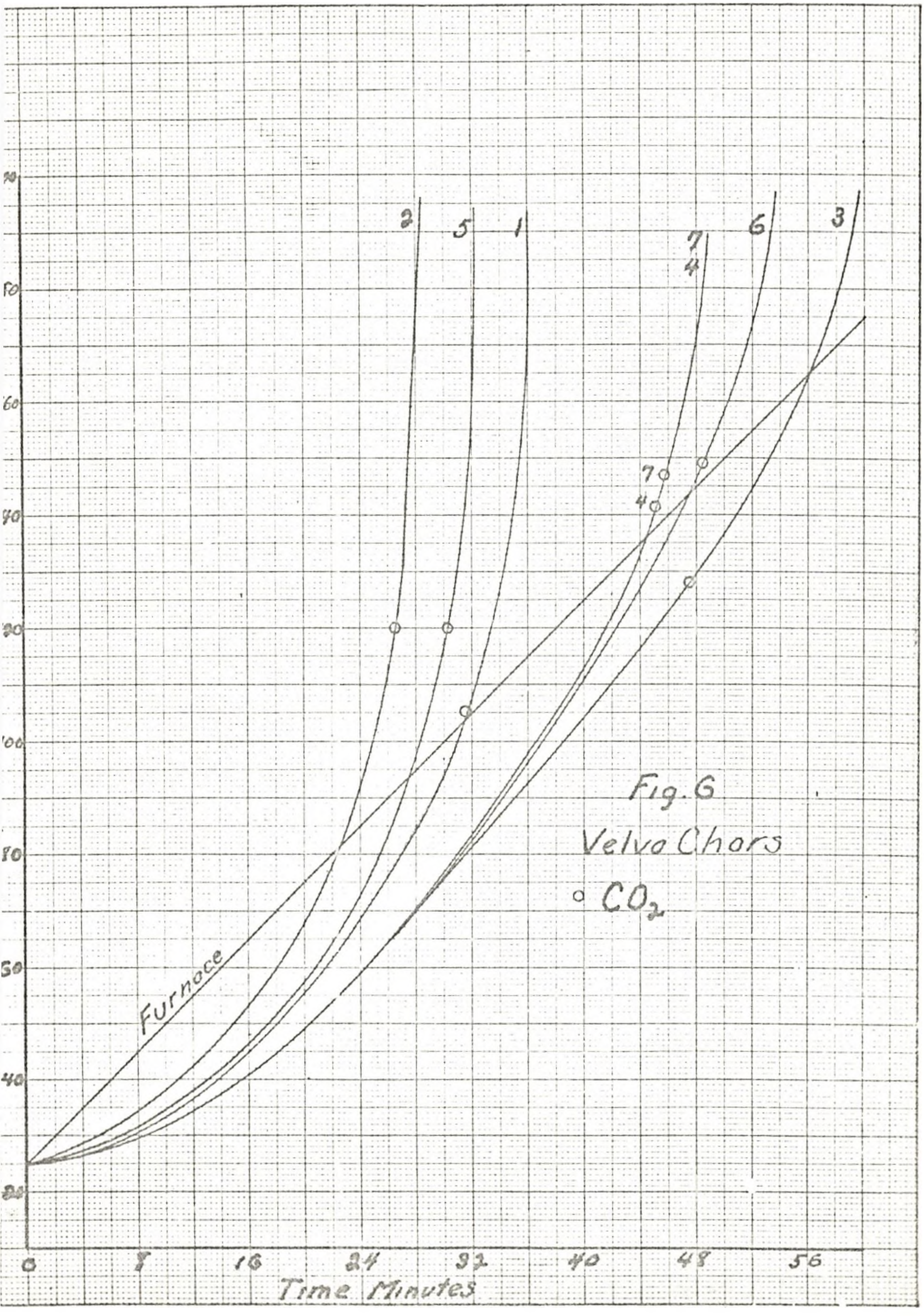

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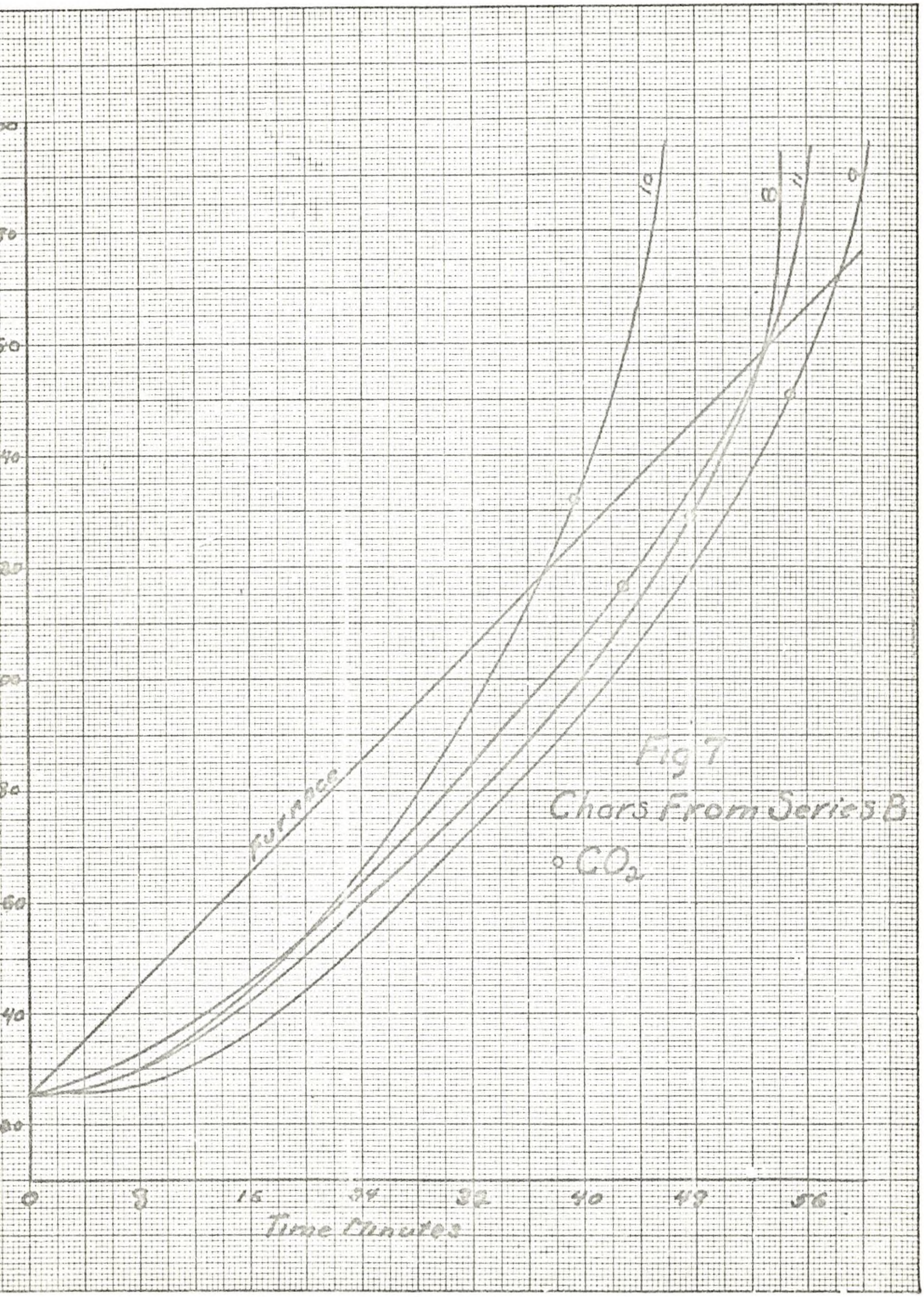

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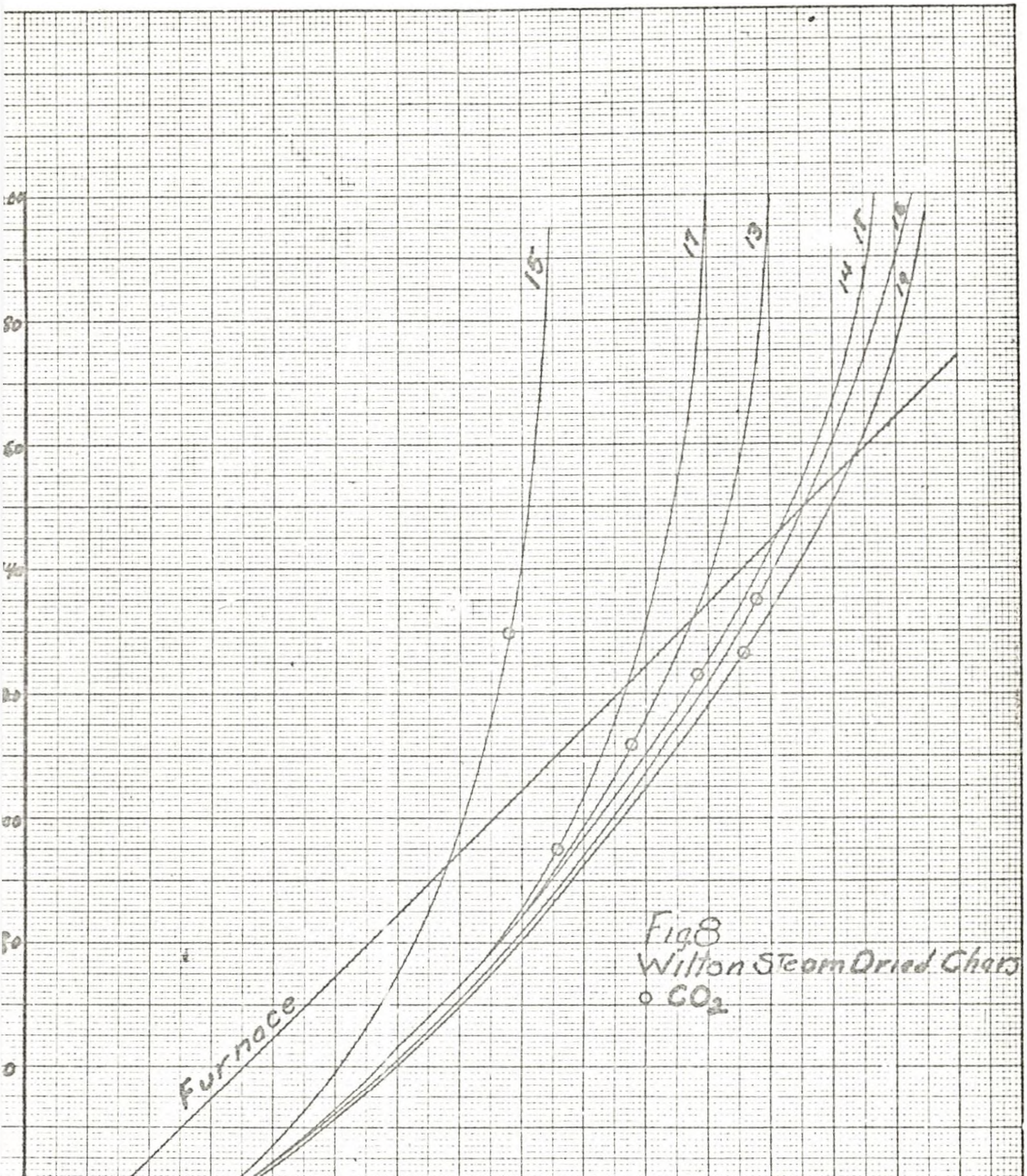

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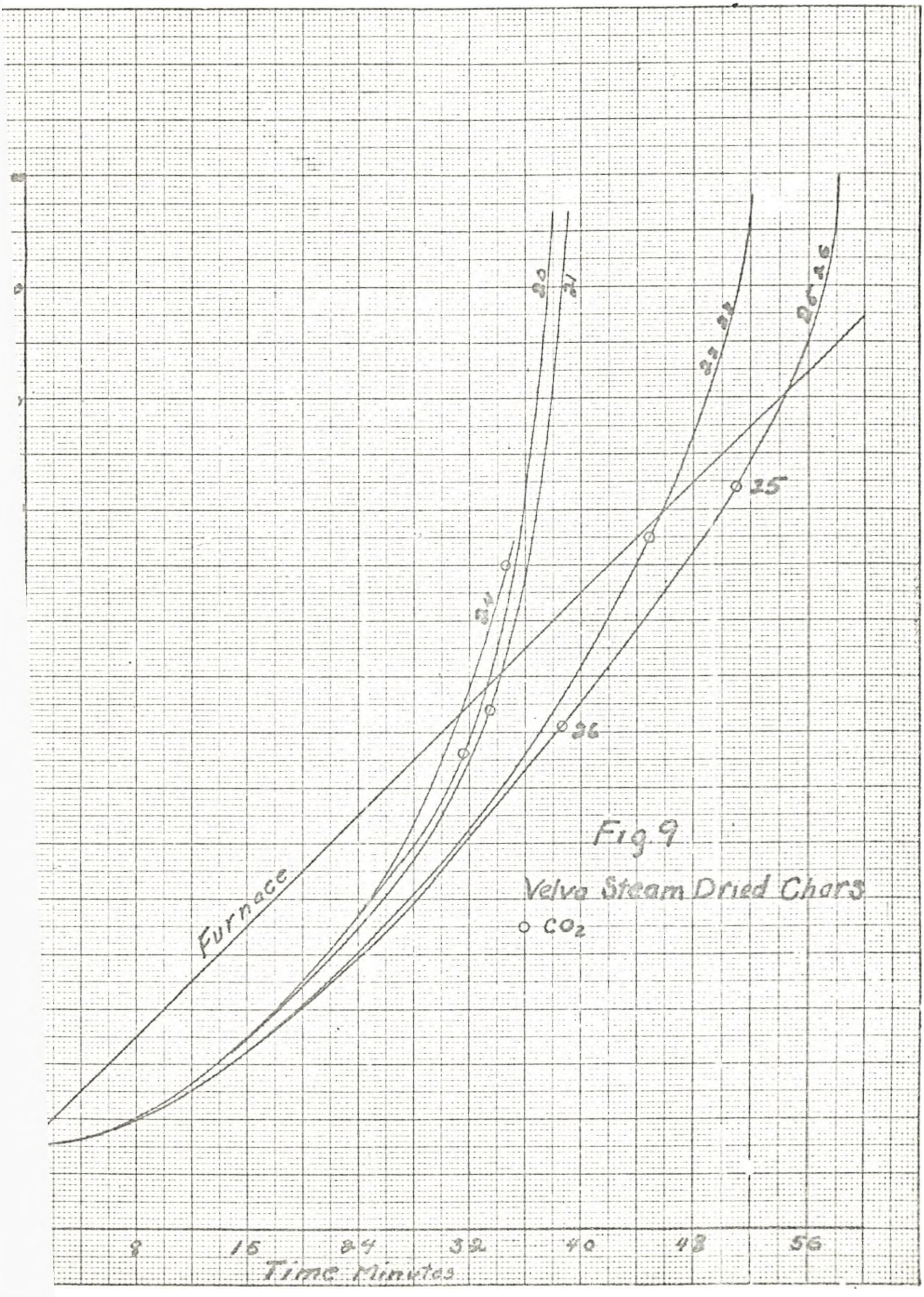

Results and Discussion:

Tables 24-28 and figures 6-9 summarize the results of this work (mixture numbers and curve numbers refer to the mixtures used in table 2, part 1.).

Chars from freshly mined coal.

An inspection of table 24 shows that the effect of sodium and calcium carbonate is to lower the crossing temperature and give a much more reactive char. King and Jones (21) and Branson and Cobb (22), using the decomposition of carbon dioxide at higher temperatures as an index to reactivity, find that sodium and calcium carbonate increase the reactivity values for coking coals. Obviously a direct comparison cannot be made because of the difference in methods. However a relative comparison can be made.

The addition of Iron Chloride hydrate and magnesium chloride hydrate results in lowering the reactivity values about the same amount. King and Jones (21) find that the addition of magnesium oxide is practically without effect. In the addition of iron oxide we find an increase in reactivity for coking coals, which agrees with the work of Branson and Cobb (22).

Aluminum chloride and sulfate hydrade give the least reactive materials but the best cokes. This may be due to the carbon taking on of a different form or the particles become coated from the secondary decomposition with carbon which decreases the active surface.

Effect of Extraction with Hydrochloric Acid and Sodium Hydroxide:

A study of the data for the extracted coals in table 25 (mixture 8 and 9) shows the effect of washing with hydrochloric acid. The char obtained without addition of inorganic material is low in reactivity when compared with the blank from the freshly mined coal. The addition of aluminum sulfate hydrate further decreases the reactivity but not to the same degree as it did for the freshly mined coal.

The effect of removing some of humates (mixture 10) is to decrease the reactivity when compared with freshly mined coal (blank). The addition of 10 per cent humic acid (mixture 12) to freshly mined coal decreases the reactivity. From these results it would indicate that humic acid present before carbonization does not have any effect upon the reactivity of the resulting char, yet it must be remembered that the extraction with sodium hydroxide effects the ash content which may offset the effect of the extracted humic acid.

Effect of steam drying.

A comparison of the data in table 27 (figure 6) with the data given in table 24 (figure 9) shows that steam drying may have a decided effect on the reactivity, both with and without addition of inorganic salts. The general effect of steam drying is to cause a decrease in the activity of char carbonized without addition of inorganic salts. Sodium and calcium carbonate do not give the wide deviation they gave in the freshly mined coal. The hydrates of magnesium chloride, aluminum chloride, aluminum sulfate, and ferric chloride give lower reactivity values for steam dried than freshly mined coal.

An inspection of figures 6 and 9 shows that, with the exception of aluminum sulfate hydrate, carbon dioxide is not liberated until after the crossing temperature had been reached whereas the steam dried chars the carbondioxide is liberated below the crossing temperature, the sodium carbonate char is an exception to this.

Impregnated Sodium Carbonated Char.

The effect of Sodium carbonate on the reactivity of a prepared char was studied in one experiment by treating a sample of char (blank) with a solution of sodium carbonate. The proper amount of sodium carbonate was dissolved in water and the solution mixed thoroughly with the blank char. A second portion of the blank char was treated with an equal volume of water for purposes of comparison. Both samples were dried at 1050 in a stream of Nitrogen and bottled. The results are given below.

	Crossing temperature °C.	CO_2 temperature °C
Blank	155	124
	156	120
Impregated)	142	108
NA_2CO_3)	143	105
Char)		

The above table shows that the mere presence of the salt has a decided effect on the reactivity, but not to the same extent as when it is present during carbonization.

Effect of Particle Size on the Reactivity.

Combustion being a surface phenomenon and for a given volume of char the surface is a function of the particle size. It was thought desirable to investigate the relation between the reactivity and particle size. Char prepared from velva steam dried lignite with aluminum sulfate hydrate was used in the investigation. The results are given in following table and figure 10.

Particle size Mesh	Crossing temperature °C	Carbondioxide temperature °C
-20 + 40	154	109
-60 + 80	169	107
-100 + 150	179	109
-200	183	106

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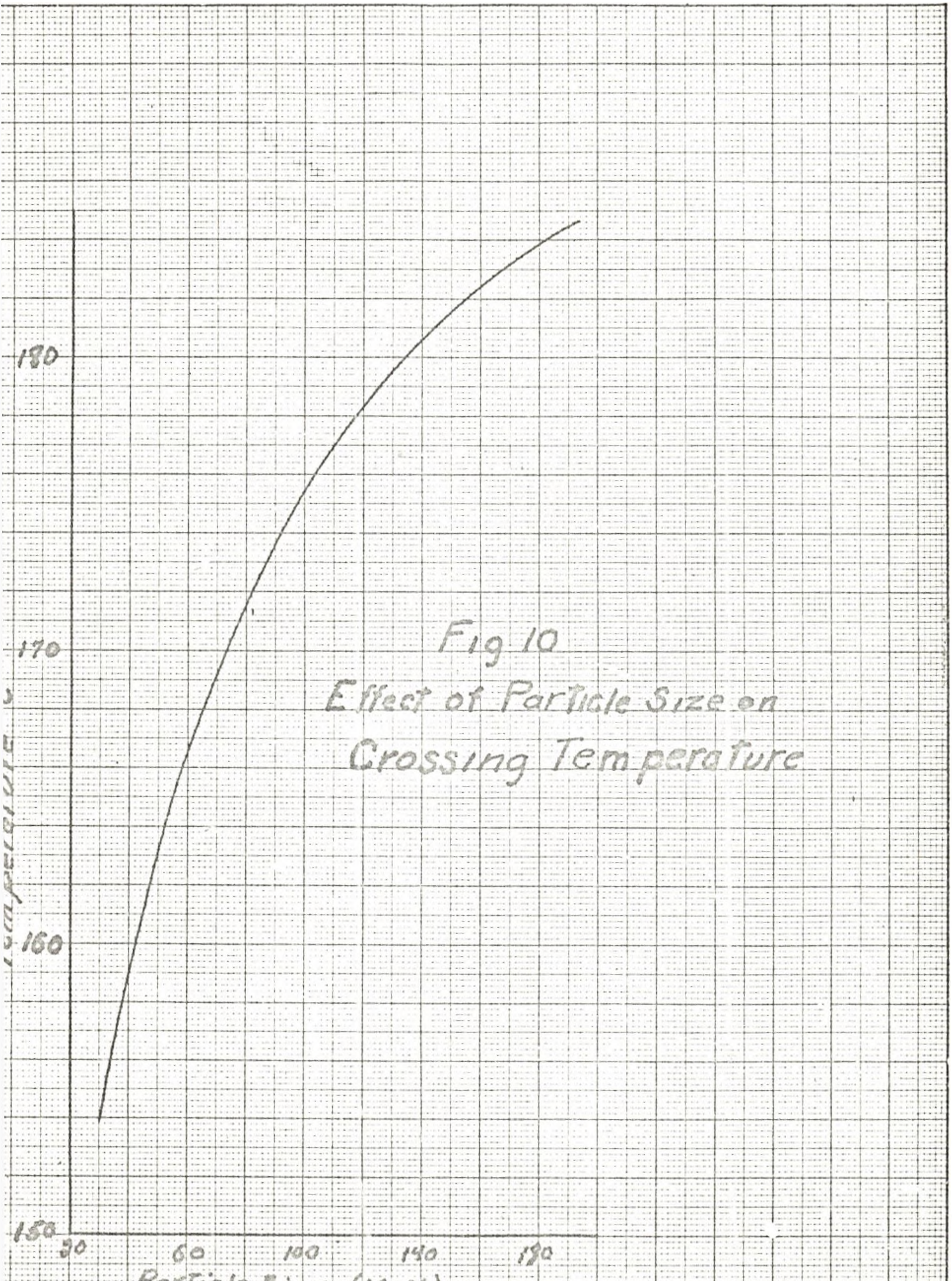

Fig 10
Effect of Particle Size on Crossing Temperature

Summary:

1. Inorganic materials have a definite effect on the reactivity of the chars from North Dakota lignite.
2. Steam drying before carbonization decreases the reactivity.
3. Particle size has a definite effect on reactivity.

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